

PHOTOCHEMICAL REACTIONS OF 1-PHENYLPHOSPHOLE OXIDE DIMER

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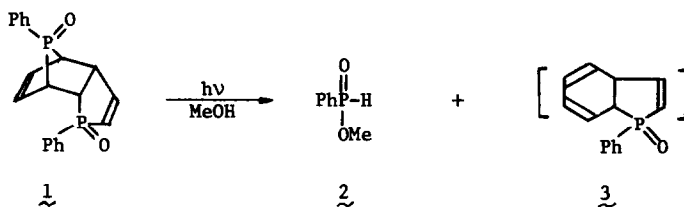
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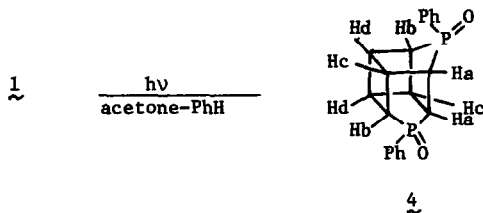
In view of the novel photochemical pericyclic fragmentation of 1-phenyl-3-phospholene oxides in our previous investigation,¹ we have examined the photochemical behaviour of 1-phenylphosphole oxide dimer (1) and found that both the singlet and triplet excited states of 1 are chemically reactive but lead to entirely different products.

Direct irradiation² of 1 (0.9g) in methanol (150ml) for 1 hr. gave a 60% yield of methyl phenylphosphinate (2)¹ as a sole isolable product. However, all attempts to isolate and/or trap dihydrophosphindole (3) as a possible resulting product from phosphinidene oxide extrusion were unsuccessful at the present stage. Efficient fragmentation of 1 might



be necessarily nonlinear disrotatory process, if concerted, because of the geometrical requirements of the fused ring system, which is consistent with our previous observation³ that cis,cis-2,5-dimethyl-1-phenyl-3-phospholene oxide cleaved efficiently in nonlinear disrotatory mode to yield trans,trans-2,4-hexadiene.

Sensitized irradiation² of 1 (1.0g) in 1:3 acetone-benzene (240ml) for 2 hrs., on the other hand, produced a cage product (4) in nearly quantitative yield: mp 249-250° (recrystallized from CHCl₃-pet. ether after column chromatography on silica gel); ir (KBr) at 1440 (P-Ph) and 1182 cm⁻¹ (P=O). The n.m.r. spectrum of 4 showed, in addition to phenyl



protons at 7.38–7.88 ppm, four pairs of saturated methine protons (δ_{CDCl_3}): Ha, 3.72; Hb, 3.34; Hc, 3.10; Hd, 2.83. Further evidence on the assignments of methine protons was obtained by adding the shift reagent, tris(dipivalomethano)europium (III),⁴ to a CDCl_3 solution of $\overset{\sim}{4}$ in varying amount. The relative shifts of Ha, Hb, Hc and Hd obtained from a plot of chemical shift vs. $[\text{Eu(DPM)}_3]/[\overset{\sim}{4}]$ ratio for each of these methines were 1.00, 0.61, 0.46 and 0.38, respectively. These data are compatible⁵ with the formation of caged adduct $\overset{\sim}{4}$ by intramolecular [2 + 2] cycloaddition of the *endo* Diels-Alder adduct⁶ $\overset{\sim}{1}$, as observed⁸ in the analogous photochemical cycloaddition of cyclopentadienone dimer.

References and Footnotes

1. H. Tomioka, Y. Hirano and Y. Izawa, *Tetrahedron Lett.*, 1865 (1974).
2. All irradiations were carried out under N_2 in an immersion apparatus using a quartz well and a 300 watt high pressure Hg lamp.
3. H. Tomioka and Y. Izawa, to be published.
4. For previous use of this shift reagent in n.m.r. studies of cyclic phosphine oxides, see R. B. Wetzel and G. L. Kenyon, *J. Amer. Chem. Soc.*, **94**, 9230 (1972).
5. Elemental analysis also supported the structure.
6. The *endo* ring juncture has been shown⁷ for a 1-ethoxyphosphole oxide dimer.
7. Y. H. Chiu and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **91**, 4150 (1969).
8. E. Baggolini, E. G. Herzog, S. Iwasaki, R. Schorta and K. Schaffner, *Helv. Chim. Acta*, **50**, 297 (1967).